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Viewpoint set

Strengthening mechanisms in high entropy alloys: Fundamental issues

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ABSTRACT

High entropy alloys (HEAs), offering a multi-dimensional compositional space, provide almost limitless design opportunities surpassing the frontiers of structural materials development. However, an in-depth appraisal of the fundamental materials physics behind strengthening in HEAs is essential in order to leverage them to achieve greater flexibility in application oriented materials design. This viewpoint paper concentrates on issues regarding inherent compositional fluctuations in HEAs and corresponding impact on strengthening is highlighted. In particular, metal physics based design criteria in multi-phase HEAs are discussed and comparisons between multi-phase and single-phase HEAs are drawn.

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1. Introduction

Most conventional metals and alloys display a trade-off effect associated with their strength-ductility values, often highlighted by the well-known banana-shaped variation of strength vs. ductility. In other words, strength increment in metallic alloys is often associated with simultaneous reduction in ductility and vice-versa [1–3]. In this regard, one of the critical research problems in the area of structural materials is to design materials that successfully evade this inverse strength-ductility relationship [4,5]. To achieve this for conventional alloys, the most potent design aspect still pertains to exploiting the local scale compositional and microstructural heterogeneities, wherein different phases or grain orientations display varying elastic stiffness and strain accommodation mechanisms. By appropriate thermo-mechanical processing, a non-homogeneous composite like mechanical response can be triggered such that different regions in the microstructure contribute to strengthening and higher ductility, respectively [5]. However, when considering dilute conventional alloys, where a well-defined solvent matrix is present in addition to low alloying amounts of different solute elements, the possibility to generate significant and diverse phase heterogeneities at multiple length scales becomes quite difficult or rather impossible to achieve.

The last decade has seen emergence of a newly developed class of High Entropy Alloys (HEAs) or multicomponent alloys

that ideally comprise of equiatomic or near equiatomic proportions of four to five elements, giving rise to a single-phase solid solution [6,7]. The concept of achieving a single-phase matrix, despite the absence of well-defined solvent, is based upon the precedence of entropic stabilization over enthalpy contributions of the expected intermetallic phase formations [7]. However, the current state of the art with regards to design of HEAs reveals that the majority of the alloys fabricated exist either as multi-phase or the known single phase compositions decompose over long durations into more than one phases [8–14]. This is owing to the significant compositional fluctuations and phase reordering during the thermomechanical processing and subsequent room temperature characterization of these alloys [14–16].

While the search for single-phase random HEAs is still being pursued using combinatorial approach methodologies [17–19], significant interest has been generated in designing high strength-high ductility multiphase HEAs [4,11,20–23]. The underlying reason being greater degree of freedom in exploiting the compositional space over conventional alloys, whereby multi-scale heterogeneities can be tailored in terms of both alloying chemistry and crystallographic defect distribution.

The current viewpoint paper, hence, presents the key metal physics behind strengthening and related microstructural design possibilities in HEAs. An insight into the theoretical models of solid solution strengthening in HEAs is briefly discussed, along with emphasis upon the inherent limitations of application of such models for currently existing HEAs, which are far away from random solid solutions. Moreover, the inadequacies with respect to predicting strengthening solely based upon solute induced lattice friction hardening and the need of alternative strengthening contributions

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is highlighted. The article further critically discusses strengthening aspects in multiphase HEAs and design pathways for structurally advanced HEAs. Finally, a clear advantage of multi-phase HEA nano/microstructures that trigger multi-scale strengthening over single-phase HEAs in terms of overall mechanical response will be justified.

2. Theoretical solid solution strengthening models in HEAs

In general, HEAs are supposed to represent random solid-solution alloys with many components [7,24]. To a certain extent it is accepted that solid solution hardening is one of the principal causes of the exceptional mechanical properties of HEAs [25]. The high yield strength of some HEAs is mainly related to the solid solution strengthening and interface strengthening effects. In some systems the contributions to yield strength and interface strengthening showed to be equally distributed, i.e. half of its value is due to interface/ grain-boundary strengthening and the other half is caused by solid solution hardening effect.

Despite the obvious importance of solid solution to the strengthening of metallic alloys, it is not so obvious how to describe the physical mechanisms behind these phenomena in case of concentrated alloys. A couple of points were clarified recently and a number of critical issues are mentioned in the following [26–38]. Solid solution strengthening in metallic alloys manifests due to either direct or indirect interactions between solute atoms and dislocations. When an incoming dislocation approaches the vicinity of a solute atom, it gives rise to the following dislocation/solute interactions: Elastic stress field of the solute and dislocation interact as well as the line energy of the dislocation is modified owing to the difference in atomic sizes and shear moduli of the solute and solvent; Contributions from the changing interatomic bonding environments due to presence of solutes inside dislocation core and stacking faults also referred to as ‘Suzuki’ strengthening effect.

From a classical perspective, the type of obstacles can be broadly divided into categories depending on the range of interactions. Fleischer [39] and Friedel [40] were the first to postulate independently that isolated solutes atoms act as direct pinning agents. In the words of Fred Kocks, Ali Argon and Mike Ashby [41], “discrete obstacles describe obstacles to slip whose dimensions are limited in both directions in the slip plane (although not necessarily perpendicular to it). The limits of the obstacles do not have to be sharp, they merely must be sharp enough for it to be treated as an individual”. Most of the theoretical concepts developed since the 1960s by Jacques Friedel, Robert Fleischer, Frank Nabarro, Reiner Labusch and later by Michael Zaiser [39,41–45] were focused on rather dilute solid solution alloys which is obviously not the case in HEAs and MEAs (Medium Entropy Alloys). Some obstacles may have long-range elastic stress fields, such as the interaction between a dislocation and the stress fields of all the other dislocations or solutes (diffuse obstacles) or interact only locally with the dislocation line (localized obstacles). In contrast to most of the (preliminary) theoretical descriptions in HEAs, in real crystals the dislocation lines are seldom straight and the obstacle will bend nearby parts of the dislocation through a large or small angle against the line tension T , described in the dimensionless Labusch-parameter:

$$\eta_0 = \frac{L_{\text{obs}}}{\Lambda} \sqrt{\frac{2T}{F_{\text{max}}}} \quad (1)$$

where F_{max} denotes the maximum applied force that the obstacle can resist; L_{obs} is the range of interaction and Λ is the mean obstacle spacing in the slip plane. When $\eta_0 < 1$, the interaction of the dislocation line with the obstacle takes place over a small

segment and the interaction is then considered to be a point force. In that case an effective obstacle strength can be calculated as was first derived by Friedel [40]. In steady state, Friedel statistics assume that a dislocation released at one obstacle must, on average pick up exactly one on another site. However, from a comparison between experimental in-situ pulsed- nuclear magnetic resonance and the values predicted using Friedel statistics, it can be concluded that in each dislocation jump a number of effective solute atoms (several orders of magnitude bigger than unity) is bypassed [46–48]. These experiments based on spin-lattice relaxation measurements show that fluctuations in the quadrupolar field caused by moving dislocations in alloys are very different from those in ultra-pure metallic systems. We do not intend to summarize all details in this contribution but the basic idea is that dislocations (in cubic systems, like FCC and BCC) have a disturbed cubic symmetry around the core and therefore dislocations possess non-zero components of the (electric) field gradients at the nuclei. In crystals the individual atoms or ions are assumed to have spherical symmetry in a first approximation. Thus the electric field gradients due to their own electron cloud vanish and the electric field gradients at a nucleus in the lattice originate from neighboring atoms. As a consequence through the interactions of the non-zero electric field gradients V_{-q}^i around dislocations and the nuclear electric quadrupole moment \hat{Q}_q^i a quadrupole-field Hamiltonian \hat{H}_Q exists, provided of course that the nuclear spin $I > \frac{1}{2}$ (like Al for FCC, V for BCC) since otherwise the nuclear electric quadrupole moment \hat{Q}_q^i at the nucleus i is equal to zero and $\hat{H}_Q = 0$ anyway.

In fact \hat{H}_Q contributes to the spin-lattice relaxes time, i.e. making the relaxation between spin system and lattice reservoir more effective depending on the coupling strength between lattice and spin systems. When dislocations are forced to move in the lattice the quadrupole-field Hamiltonian fluctuates at the nuclei, since the surroundings around the nuclei changes locally when dislocations are passing by. In other words the spin-lattice relaxation rate is affected by moving dislocations due to variations in the effective quadrupole-field Hamiltonian. Therefore by measuring the spin-lattice relaxation rate (in the rotating frame $1/T_{1\rho}$, usually near magnetic resonance) in-situ, i.e. inside a magnetic field during deformation, as a function of strain rate the mean free path can be measured directly. The fundamental idea here is to correlate the measurable spin-lattice relaxation time to the applied strain rate using the Orowan equation, i.e. to get experimental values of the waiting/run times of mobile dislocations, of mobile dislocation densities and of mean jump distances (for more details reference is made to [46–48]).

Both the spin-lattice relaxation data and the data obtained from strain-rate change experiments on several alloy systems indicate that Friedel’s approximation of solution hardening is violated and is not applicable, neither in dilute or concentrated HEAs. In fact, only fairly strong obstacles at very low concentrations seem to fall inside the range where Friedel’s model is justified. Rather, that physical description seems to work for describing the interaction between moving dislocations and forest dislocations, not for solutes and definitely not for HEA/MEAs.

When $\eta_0 > 1$, diffuse obstacles are assumed to create an average stress τ_i in a region of size Λ , the average obstacle spacing. The diffuse forces bend the dislocation line into an arc of radius R against the line tension T . The physical picture given by Nabarro underlying the Labusch derivation is that of a mean fluctuation in the sign of the obstacle interaction, positive and negative, whereas in the Friedel picture, all obstacles are repulsive. For rather strong diffuse obstacles, the radii of the arcs into which the dislocation line is bent are of the order of the obstacle spacing, Λ . The flow stress is that required to overcome the mean internal stress: $\bar{\tau} = \bar{F}/bL_{\text{obs}}$, where \bar{F} denotes the average Peach-Koehler force due

to the interaction between the dislocation line and the obstacles:

$$\tau_{\max} = \sqrt{\frac{2}{\pi}} \left(\frac{L_{\text{obs}}}{\Lambda} \right)^{1/3} \frac{\bar{F}}{b\Lambda} \quad (2)$$

Mathematically, the strengthening from isolated solutes varies as a function of $c_i^{0.5}$ vis-à-vis for diffuse obstacles where the strengthening scales as a function of $c_i^{0.66}$, where c_i is the solute content.

In context with MEAs/HEAs, it is important to reiterate that these models were primarily developed to gauge the solute strengthening response in conventional alloys i.e. for dilute alloys. In that respect, the scenario is expected to be much more complicated when applying the aforementioned approach in the case of highly concentrated alloys such as HEAs, wherein an accurate demarcation between solute and solvent cannot be established anymore. A dislocation pinned at, due to size effects, different obstacles in HEAs may “unzip” along its entire length after thermal activation of only one segment of the dislocation across the barrier, since at that very moment the critical breakaway angle of all other segments might be exceeded.

First attempts for a theoretical assessment of solid solution strengthening in single phase HEAs were made by Toda-Caraballo and Rivera-Díaz-del-Castillo [35,36], which was essentially an extension of the Labusch type model for conventional alloys that considers a random distribution of solute atoms as diffuse obstacles for dislocation motion. The misfit in atomic size contribution is calculated by measuring individual interatomic spacing with respect to the mean lattice parameter obtained through averaging all interatomic spacing between like-like and like-unlike elements in the alloy. In the same way, the modulus misfit is measured over a reference value that corresponds to a mean shear modulus for the HEA as obtained from the weighted average of individual shear moduli contributions of each alloying element.

Solid solution strengthening mechanisms in random FCC alloys were also theoretically evaluated by Curtin and co-workers, wherein an effective medium-based strengthening model was established [37]. Each element is considered as a solute in a mean field solvent, which is described by the averaged properties of the alloy i.e. lattice spacing, elastic constants and stable and unstable stacking fault energies. In comparison to the model proposed by Toda-Caraballo and Rivera-Díaz-del-Castillo, the effective medium-based strengthening theory also reintroduced the influence of stress field fluctuations due to the presence of solutes on the dislocation line tension, thereby also considering the effect of mesoscopic stress fluctuations on the solute hardening response. In contrast to the general ideas around HEAs the work leads to the surprising findings that the strength does not directly depend on the number of components, and is not maximized by the equi-atomic composition. In particular, the strongest and most temperature-insensitive materials are achieved by maximizing the concentration-weighted mean-square misfit volume quantity and/or increasing the shear modulus.

Despite the fact that the aforementioned theoretical models provide interesting insights on the role of lattice distortion on yield strength increment in HEAs, application of these models to experimentally designed HEAs possesses a major limitation with respect to complete determination of the strengthening response. In particular, the assumption of a random solid solution HEAs in the abovementioned models is practically difficult to achieve owing to the enthalpy driven phase reordering or separation during thermomechanical processing in most HEA microstructures [14]. Such correlated atomic rearrangements invariably lead to strong compositional fluctuations that either display short-range or long-range order, wherein confounding effects of solute clusters/secondary phases adulterate the pure solid solution strengthening response. This notion also obviates the commonly

postulated assertion that HEAs or concentrated alloys would ideally be stronger than conventional alloys owing to enhanced solid solution strengthening. Consequently, the impact of such local chemical ordering on dislocation motion becomes a critical aspect that needs to be evaluated and strengthening models purely based upon lattice friction induced hardening would not hold valid for most of the currently existing HEAs.

In fact this was corroborated by the findings in a recent study by Robert Maaß and collaborators, wherein the peak dislocation velocities in FCC $\text{Al}_{0.3}\text{CoCrFeNi}$ and pure Au did not show much difference, indicating dislocation motion is not significantly sluggish in single phase solid solution HEAs (Rizzardi et al. [49]). In light of the aforementioned aspects, it becomes necessary to appraise both independent and interdependent effects of crystallographic defect (i.e. both line and planar defects) topology and compositional fluctuations on the local strengthening response.

A detailed analysis of the strain hardening behavior in several of these HEAs indicates that the presence of ‘multiple solutes and solvents’ does not always greatly affect the dislocation accumulation. It means that strain hardening with increasing number of components is due to an increase of the strength of dislocation/dislocation interaction; i.e. there exists some rearrangement of solutes/solvents correlated with the position of the dislocations which can occur even at ambient temperature that results in an increase in the effective dislocation/dislocation strength. This may result in a multiplicative effect of solutes/solvents on strain hardening (see also [46]).

3. Alternative strengthening contributions in HEAs

The multicomponent nature of HEAs leads to significant frustration in the resultant crystal structure. One of the direct outcomes of such complexity in crystal structure is that the characteristics of overall plasticity in HEAs can be quite distinct in comparison with conventional alloys. In particular, the inherent compositional fluctuations in these multicomponent alloys can give rise to local heterogeneities in the microstructures that can span across multiple length scales. Ranging from the influence of local chemical ordering effects, either short- or medium range, at atomic scales to phase interface generation through phase separation mechanisms at sub-micron/ nanoscales, these compositional fluctuations play a definitive role in the overall defect configurations in HEAs i.e. phase/grain boundaries, twin boundaries, dislocations [4,14]. Broadly speaking, strengthening and strain hardening in most non-random and multi-phase HEAs find contributions from heterogeneities at the following levels:

- At the first order, the local chemical ordering effects at the atomic-scale significantly alters the ease of dislocation motion as well as the dislocation line energy, wherein mutual interactions between dislocation stress fields that constitute a major component of stage II hardening behavior is modified.
- At the nanometric level, ordered cluster formations and nano-sized precipitates that give rise to coherency strain fields and precipitation hardening effects with sizable back stresses on dislocation motion during plasticity
- At a more advanced stage of precipitation, presence of ordered secondary phases or spinodally modulated structures give rise to large density of interphase boundaries and subsequent strengthening contributions in form order hardening, spinodal strengthening etc.
- At larger length scales, sub-micron/micrometer scales, defect structures such as grain boundaries, crystallographically dissimilar phase boundaries, and twin boundaries strongly interact with line defects, and influence the strengthening and plasticity response.

Hence, engineering nanostructured heterogeneities (both compositional and in defect distribution) in HEAs can be utilized as a potent mode to enhance strength and ductility simultaneously, whereby simultaneous activation of multiple strengthening contributions is activated. In light of the aforementioned arguments, the role of HEA chemistry on the following strengthening mechanisms needs to be critically assessed when considering design of structurally advanced alloys for future applications.

3.1. Influence of stacking fault energies in HEAs

It has been shown previously [50–52] that the propensity of local chemical ordering in HEAs has direct influence on intrinsic and extrinsic stacking fault energies (γ_{SFE}). Physically, γ_{SFE} describes the energy required to disrupt the existing atomic stacking sequence on a crystallographic plane and directly correlates to dislocation nucleation and mobility. It is well known that the magnitude of γ_{SFE} in materials governs the mechanics of deformation ranging from twinning dominated at low values to slip mediated at large γ_{SFE} values. Using Density Functional Theory (DFT) simulations, Ritchie and co-workers showed that tuning local chemical ordering in CoCrNi resulted in a variation of intrinsic and extrinsic γ_{SFE} values ranging from -43 to 30 mJ m^{-2} and -28 to 66 mJ m^{-2} , respectively [50]. Fig. 1a shows the variation in stacking fault energy distribution with local chemical ordering, with CH_0 defined as random state and CH_F indicates the final state with solute clustering. Intermediate stages are represented by CH_1 and CH_2. In another study Ritchie and co-workers [51], illustrated that changing γ_{SFE} shows distinct variation in the deformation response when comparing CoCrFeNiPd ($\gamma_{\text{SFE}} = 66 \text{ mJ m}^{-2}$) with the well-known CoCrFeMnNi cantor alloy ($\gamma_{\text{SFE}} = 30 \text{ mJ m}^{-2}$). While the former HEA alloy displaying greater chemical ordering effects showed cross-slip mediated plasticity and hindered dislocation motion, the FCC Cantor alloy revealed highly active splitting of $\frac{1}{2}110\{111\}$ full dislocation into $\frac{1}{6}112\{111\}$ Shockley partials. The stark difference in deformation mechanisms manifests as higher strength and greater work hardening in the CoCrFeMnNiPd alloy vis-à-vis CoCrFeMnNi (c.f. Fig. 1b). In an independent study, Zhang et al. [52] revealed that the exceptional ductility of high entropy alloys in cryogenic temperatures is attributed to negative stacking fault energies whereby profuse generation of stacking faults and nano-twins dictate the plasticity response. Presence of a large density of stacking faults can significantly augment the intra-granular strain hardening response in HEAs due to strong dislocation-stacking fault entanglements and creation of large density of partial dislocations. In addition, the local chemical ordering combined compositional gradients leads to large variation in stacking fault widths inside the same alloy, whereby the dislocation line configuration will be much wavier and complex resulting in hindered mobility. Activation of such mechanisms would invariably augment the generic strain hardening response in comparison with single-phase random solid solution HEAs as well as conventional alloys. Hence altering γ_{SFE} via. compositional tuning through local ordering and clustering provides a great platform to mechanistically design high strength – high ductility HEAs.

In light of the aforementioned theories, one such potential alloy design pathway employs compositional fluctuations as a means to intrinsically modify γ_{SFE} and trigger additional strain accommodation mechanisms such as deformation twinning induced plasticity (TWIP) phenomenon. Twinning not only contributes to plasticity but also can promote dynamic Hall-Petch driven strengthening behavior, owing to grain fragmentation through twin boundary formation. TWIP effects were observed in a non-equiatomic $\text{Fe}_{40}\text{Mn}_{40}\text{Co}_{10}\text{Cr}_{10}$ HEA at higher deformation strains, whereby a significant enhancement in the overall strength-ductility response

was observed [53]. In recent work [54] it was shown that by modifying the composition of Mn from 50% to 10% in the CoCrFeMnNi cantor alloy, the mechanical response varies from dislocation and slip induced microband dominated deformation for high Mn content (large γ_{SFE}) to nano-twinning based deformation at low Mn contents (small γ_{SFE}). While the former contributes to higher work hardening, the latter optimizes hardening with enhanced ductility. It becomes of interest to pursue alloy design strategies that can trigger composition gradients in Mn content such as using diffusion couples, wherein a bimodal deformation scheme combining high hardenability associated micro-banding phenomenon and simultaneous ductility and grain boundary strengthening from nano-twinning is achieved.

3.2. Transformation induced plasticity effects

Chemical gradients in HEAs are instrumental in triggering local rearrangements and shuffling of elements thus influencing the stability of the existing phases. A direct consequence of such local elemental heterogeneities manifests as a greater susceptibility of HEAs to undergo dynamic phase transformation under applied temperature or stress, which could serve as potent mechanism to trigger interesting plasticity mechanisms as well as accommodate larger strains. Li et al. demonstrated for non-equiatomic compositions [11] based on the FCC single phase Cantor alloy, dynamic transformation of FCC to HCP crystal structure during plastic deformation was observed that simultaneously enhanced strength and ductility. Basu et al. [21] reported dynamic indentation induced phase transition from BCC to FCC in $\text{Al}_{0.7}\text{CoCrFeNi}$ HEAs (c.f. Fig. 1c). The transformation was attributed to the metastability of A2 phases owing to local compositional fluctuations of Al in the spinodally decomposed BCC phase such that under applied stress the A2 phases that were locally depleted in Al content could displacively transform to the more stable and ductile FCC phase.

The results once again provide an opportunity for exploiting compositional fluctuations in tandem with thermomechanical treatment that dynamically generates strength and ductility enhancing mechanisms. Displacive phase transformation effects or TRIP effects in HEAs could be exciting focal points in novel advances of HEAs in structural properties and applications. Another lucrative pathway would be to utilize the compositional gradients in HEAs to activate simultaneous TWIP-TRIP effects. Simultaneous TWIP/TRIP activation not only results in dynamic generation of interfaces as well as contributes to more complex interphase dependent dislocation-boundary interactions (that will be discussed later on) both of which promote strain hardening and interface strengthening. For instance, it was shown for non-equiatomic FeMnCoCr alloy when combined with dilute additions of C (~0.6 at%) simultaneous twinning and phase transformation is triggered along with interstitial hardening response [55]. In another study, non-equiatomic BCC TiZrHfNbTa , when strained, undergoes displacive transformation from BCC to HCP phase, with the latter phase exhibiting deformation twinning [56].

3.3. Interphase dependent strengthening in HEAs

Thirdly, the influence of alloying chemistry on engineering interphase boundaries in HEAs, rather than only focusing upon solid solution strengthening as the primary strength contributor in these alloys, needs to be looked upon in detail. The prospects of utilizing long-range compositional gradients to generate interphase boundaries in the microstructure can significantly enhance the overall strengthening response. One of the model HEAs in this regard is the well-established multicomponent $\text{Al}_x\text{CoCrFeNi}$ alloy. In a recent work, it was shown that the well-established spinodal decomposition of BCC phase of high Al-containing $\text{Al}_{0.7}\text{CoCrFeNi}$ HEA

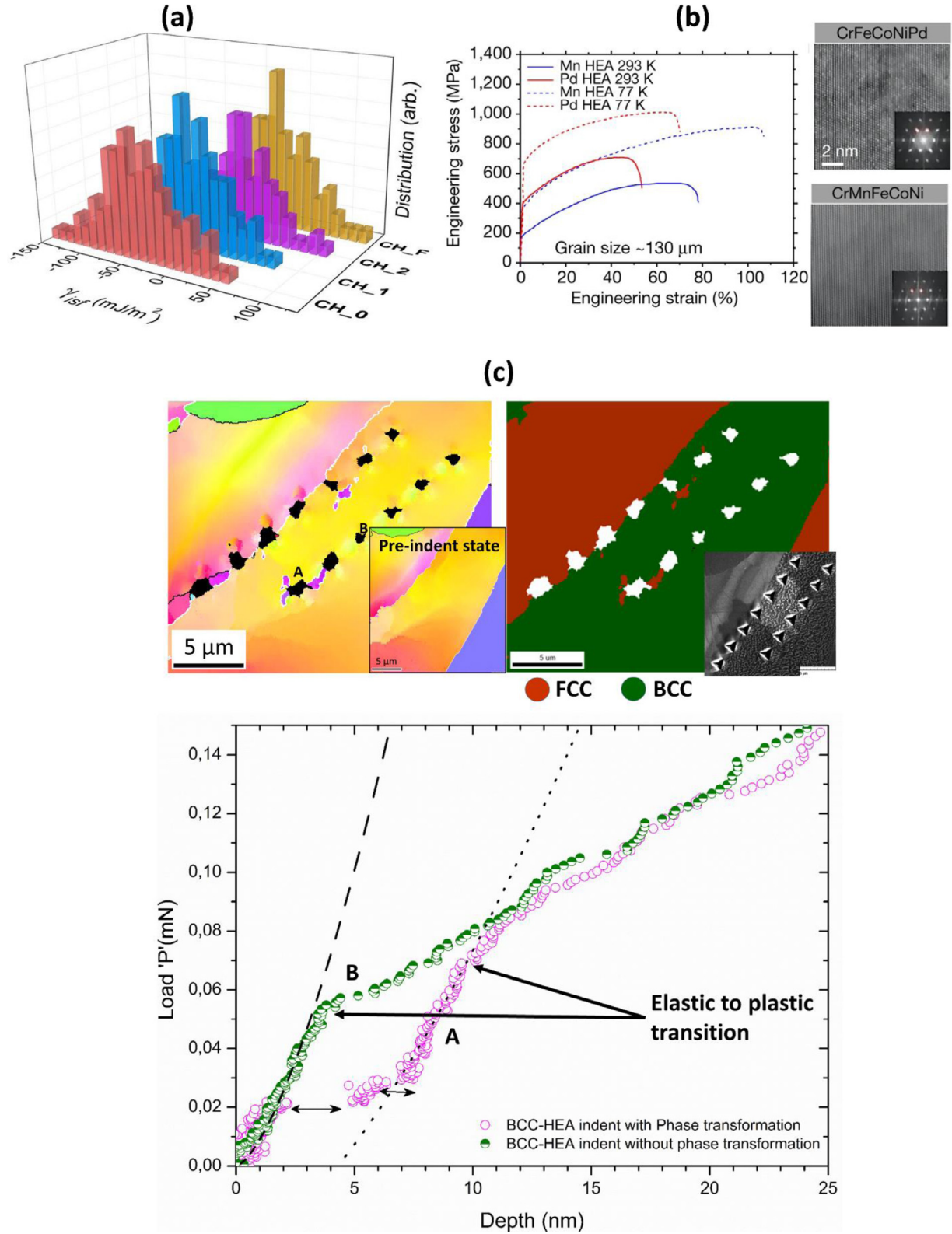


Fig. 1. (a) Variation of intrinsic stacking fault, γ_{isf} as a function of local chemical ordering. The four states shown as CH_0, CH_1, CH_2 and CH_F, represent CrCoNi alloys as random solid solution (CH_0) to highest ordering (CH_F) (adapted with permission from ref. [50]); (b) Tensile stress-strain curves of CoCrFeNiPd and CoCrFeMnNi alloys at 77 K and 293 K, respectively. HAADF image and selected area diffraction patterns for CoCrFeNiPd and CoCrFeMnNi alloys, with the former showing larger atomic strain due to higher degree of atomic clustering (adapted with permission from ref. [51]); (c) Indentation induced phase transformation from BCC to FCC observed in the BCC grains in Al_{0.7}CoCrFeNi alloy; the phase transformation associated elastic strain accommodation appears as discrete displacement bursts in the load-displacement curve (adapted with permission from ref. [21]).

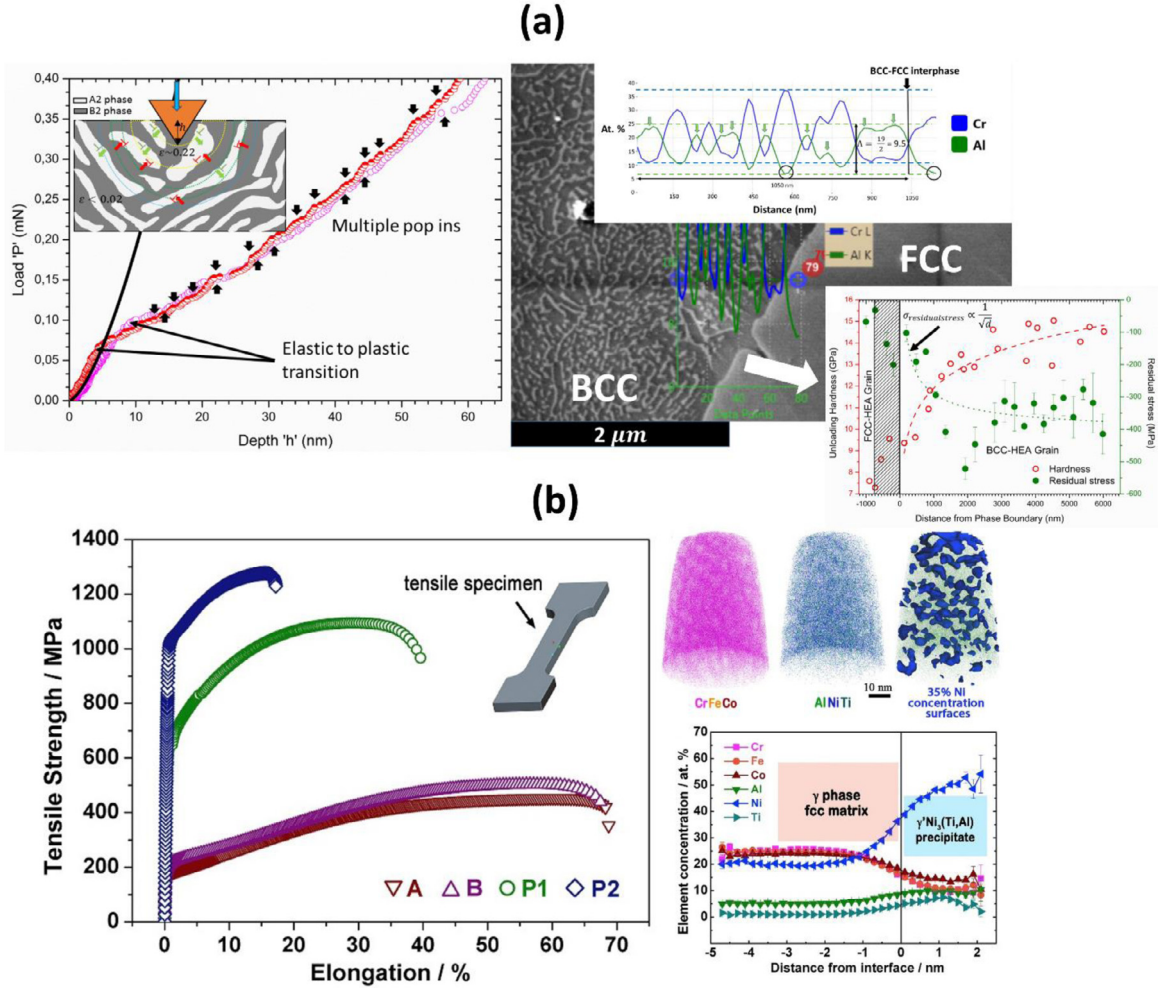


Fig. 2. (a) Spinodally strengthened BCC phase in $\text{Al}_{0.7}\text{CoCrFeNi}$ HEA displays jerky dislocation motion, indicated by serrated plastic flow; the top right image indicates the spinodally induced compositional modulation. Additionally, BCC-FCC interface contributes to simultaneous interphase boundary strengthening giving rise to large residual stresses in the BCC grain close to the interface (adapted with permissions from ref. [20,21]); (b) Effect of precipitation hardening by addition of Al and Ti to single phase FCC CoCrFeNi HEA, giving rise to tremendous tensile strength increment, without significant ductility loss. The phase contributing to the hardening mechanism are ordered coherent FCC $\text{Ni}_3(\text{Ti,Al})$ nano precipitates as seen in 3DAP elemental maps (adapted with permission from ref. [22]).

into random A2 (in light gray in Fig. 2a) and ordered B2 phases (darker phase in Fig. 2a) gives rise to simultaneous spinodal hardening and order hardening effects. Mathematically, strengthening from spinodal hardening was quantified as sum total contributions from lattice misfit effect and modulus differential, expressed as,

$$\Delta\sigma_{\text{spinodal}} = \Delta\sigma_{\varepsilon} + \Delta\sigma_G = \frac{0.5\Delta\eta E}{1-\nu} + \frac{0.65\Delta G|\mathbf{b}|}{\lambda} \quad (3)$$

where, $\eta = \frac{d(\ln a)}{dc} = \frac{\delta a}{a\delta c}$; a is the lattice constant and $\frac{\delta a}{\delta c}$ is the ratio of variation in lattice parameter between the A2 and B2 phases over the relative change in atomic concentration. E is the elastic modulus of the A2 phase and ΔG is the difference in shear moduli. Parameter λ is the mean amplitude of compositional fluctuation obtained from the EDS (Energy Dispersive X-ray Spectroscopy) line scan data in Fig. 2a and λ is the feature size of the spinodal structure. $|\mathbf{b}|$ gives the magnitude of Burgers vector of active slip-system. The effects manifest as jerky dislocation kinetics with the deformation length scales comparable to the mean size of A2 phases that is of the order of $\lambda \sim 100$ nm (c.f. indentation curves in Fig. 2a). In the case of order hardening contribution, the mathematical expression given by Brown and Ham [57] for weakly coupled dislocation pairs can be used,

$$\Delta\sigma_{\text{ordering}} = 0.8 * \frac{\gamma_{\text{APB}}}{2b} \left[\left(\frac{3\pi f}{8} \right)^{0.5} - f \right] \quad (4)$$

where γ_{APB} is the antiphase boundary energy of B2-NiAl, f is the volume fraction. The strengthening contributions from spinodal hardening and order hardening mechanisms resulted in increments of 0.5 GPa and 0.3 GPa, respectively. Mechanistic design routes based on exploiting the above described interfacial strengthening modes in HEAs recently resulted in a new generation of modulated nano-phase structures in BCC-refractory HEAs mimicking super alloy type microstructures [58,59]. Generation of spinodal order-disorder phase separated nanostructures in FCC non-equiatomic $\text{Al}_{0.5}\text{Cr}_{0.9}\text{FeNi}_{2.5}\text{V}_{0.2}$ was also shown to result in drastic strengthening and work hardening improvement in comparison to single phase FCC HEA microstructures i.e. a strength increase by ~ 1.5 GPa (560%). The adopted strategy utilized the aspect of greater compositional fluctuations by increasing the atomic ratio of Ni to Al to 5:1, whereby spinodal phase separation into random FCC and ordered L_{12} phases that are stabilized by the presence of V [60].

While spinodal HEAs put greater emphasis towards larger strengthening potential, precipitation hardened HEAs provide greater optimization in terms of beating the strength-ductility trade off or the banana curve effect observed in most metallic alloys. For instance, when considering the other spectrum of $\text{Al}_x\text{CoCrFeNi}$ alloys that is known to crystallize as single phase FCC, with low Al content ($x \leq 0.3$), it has been shown that the primary strengthening contribution is attributed to the presence

of extremely fine (~ 5 nm) ordered $L1_2$ - Ni_3Al precipitates in the aged condition that are fully coherent with the ductile FCC matrix [61,62]. The subsequent shearing of these precipitates gives rise to simultaneous precipitation hardening and order hardening effects. In reference [63], it was observed that compared to the random single-phase $Al_{0.2}CoCrFeNi$ FCC microstructure, the precipitation hardened state showed an increase in yield and ultimate tensile strength values by 259 MPa and 316 MPa, respectively without any negative compensation in elongation values. The findings clearly show the beneficial impact of dual-phase HEAs over single-phase microstructures in terms of concurrent strength-ductility increment. On similar lines, it has been seen that the addition of simultaneous addition of Al and Ti to single phase FCC $CoCrFeNi$ HEAs can also trigger precipitation hardening effects due to presence of ordered FCC precipitates, giving rise to a strengthening potential between 0.3 and 0.4 GPa [22]. Compared to the counterpart solid solution strengthening contribution, the former served as the dominant strengthening mode (c.f. Fig. 2b).

A breakthrough result in this regard was shown in the case of non-equiatomic additions of Al and Ti to $CoFeNi$ alloy leads to unprecedented strength-ductility enhancement due to a high density ($\sim 55\%$) of uniformly dispersed ordered $L1_2$ multicomponent intermetallic nanoparticles that are ductile and coherent with the FCC matrix. The resultant strengthening was as high as ~ 1.5 GPa along with remarkable ductility of the order of 50% elongation to failure strain [64].

Digressing from crystallographically similar interphases, the role of interfaces between phases crystallizing into different crystal structures could also be harnessed for activating simultaneous strength and plasticity increment. In particular, the role of dislocation-phase boundary interaction in conjunction with compositional gradients on local mechanical response needs to be addressed. The metal physics of strengthening across phase boundaries is distinct when compared with classical grain boundaries. While strain transfer across homophase interfaces is primarily governed by the geometrical alignment of incoming and outgoing dislocation slip [65–67], the strengthening across heterophase interfaces can be significantly larger as it draws contributions from additional interphase dependent strengthening modes. These alternative strengthening modes are strongly dependent upon the local compositional fluctuations and phase crystallography. Interphase dependent hardening, as has been extensively investigated in metallic multilayers [68], is known to primarily stem from three misfit effects viz.

- Elastic moduli mismatch ('image' or 'Koehler' stresses, τ_K), where the underlying effect stems from the variation of strain energy per unit length of dislocation with changing modulus. Typically, a dislocation traversing from an elastic stiffer phase into a softer phase will experience an attractive force at the interface that hypothetically equals to the stress from a negative image dislocation positioned on the other side of the interphase boundary;
- Lattice parameter mismatch ('misfit' stresses, τ_{misfit}) between crystallography dissimilar interfaces leads to the creation of a grid of interfacial dislocations that gives rise to additional coherency strain hardening effects at the interface. While the coherency stresses add up to the dislocation glide stress, they additionally strengthen non-glide stress components of the dislocation stress field by modifying the local core structure;
- Stacking fault energy (γ_{SFE}) differential or chemical mismatch effect (τ_{ch}) builds upon the above stress contribution in terms of mismatch in chemical energy or gamma surfaces. As a leading partial in a stacking fault moves across a phase interface, the dislocation configuration undergoes an abrupt change in

γ_{SFE} . The resultant change originates as an additional stress component on the leading partial.

Mechanistically, these independent magnitudes of these strengthening contributions dynamically evolve on the basis of mean distance between the incoming dislocation and the interphase; however as per continuum mechanics wherein the properties can be averaged over a single representative volume element, we can mathematically express the overall strengthening across heterophase interfaces (τ_{int}) as a linear sum,

$$\tau_{int} = \tau_{HP} + \tau_K + \tau_{misfit} + \tau_{ch} \quad (5)$$

Where, the first term on the right hand side corresponds to the interphase independent obstacle strength of the grain boundary (τ_{HP}). Local scale strengthening response was investigated across BCC/FCC interfaces in $Al_xCoCrFeNi$ HEAs based on the above parameters (c.f. lower right inset image in Fig. 2a) and it was revealed that the interfacial strengthening values across heterophase interfaces in HEAs ($\tau_{int} \sim 4$ GPa) was nearly 4 times larger than the ones observed in the case of conventional BCC/FCC interfaces [20]. The findings clearly highlight the need of further exploiting phase boundary crystallography and chemistry in multiphase HEAs as a pathway to design grain boundary strengthened damage resistance materials.

The structural benefits of a dual-phase microstructure over single phase HEAs was clearly shown in recent study [69], wherein a compositionally graded $Al_xCoCrFeNi$ bar was additively manufactured with increasing Al content from $x = 0.3$ to $x = 0.7$ along the longitudinal direction. The microstructure generated was described by a single-phase FCC crystal structure on one end of the material with the other end forming a dual phase B2-FCC microstructure. Comparing the two microstructures, the dual phase B2/FCC structure evinced the positive role of interfaces displaying a significantly larger strengthening potential.

The aforementioned strategies and examples clearly highlight the benefit of adopting multi-phase HEAs for high strength-ductility applications. An important issue that can be raised here is the relative performance of multiphase HEAs vis-à-vis single-phase HEAs. In other words, could the alloy design criterion be engineered in order to generate single-phase HEA alloys with strength-ductility enhancement in the range similar to those seen in multiphase alloys that are easily conducive to nanoscale heterogeneities in the microstructure and chemistry? In this regard, the focus lies squarely upon microstructural design in single-phase alloys and as well as modification of lattice friction response by appropriate additions of alloying elements causing a large lattice distortion. While in most cases, strengthening strategies in single phase MEAs/HEAs pursue standard strain hardening pathways through modification of grain size distribution (Hall-petch effect) and pre-existing dislocation content, evidence of strength-ductility enhancement in HEAs solely based upon solute enhanced lattice friction relative to conventional alloys is largely not observed. An outlier in this case is the reported equiatomic fine-grained $CoNiV$ MEA (grain size = $2 \mu m$) that shows a yield strength of nearly 1 GPa along with elongation to failure at 38% [70]. The primary contributions were attributed to lattice friction (higher Peierls stress) and grain boundary hardening. Despite the claims of absence of ordered phases or precipitates, the experimental evidence of local chemical ordering still needs to be considered that pertains to cluster sizes (few atoms thick) that would be difficult to detect from the HAADF-STEM (High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy) data presented in the work. Moreover, the propensity of segregation of V to the grain boundaries as shown in the 3D-atom probe tomography also alludes to possible atomic-scale clustering in the bulk. On the other hand, it is envisioned that the aforementioned $CoVNi$ alloy

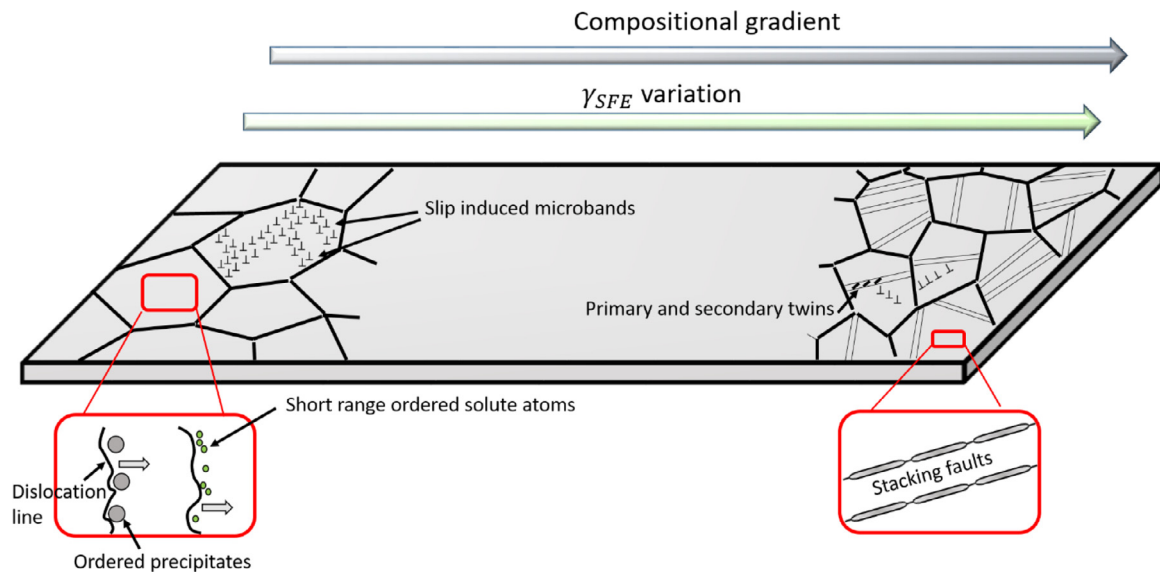


Fig. 3. Schematic showing an exemplar of gradient microstructures, with varying defect types and densities as a function of compositional fluctuations. By tailoring composition of HEAs, the phase formation tendency and stacking fault energy can be locally varied, whereby distinct deformation mechanisms are activated heterogeneously in the microstructure.

could serve as an ideal precursor for designing high strength-high ductility alloys that could involve additional interstitial and nano-precipitation induced hardening contributions.

4. Summary and outlook

To summarize, the multicomponent nature and the local compositional gradients in HEAs could be beneficially utilized to augment strengthening by inducing clustering or phase formation in existing single-phase HEAs as well as design high strength-high ductility multi-phase HEAs. The prospects of multi-phase HEAs in drawing strengthening contributions from the previously mentioned heterogeneities at different length scales in addition to the lattice friction increment makes them mechanically superior candidates than single-phase random solid solution HEAs. Such results are evident when considering the multiphase $\text{Al}_7\text{Ti}_7(\text{CoFeNi})_{86}$ HEA [60], as described earlier, that is strengthened by multicomponent nano-scale intermetallic phases giving rise to unprecedented strength-ductility increment without any thermomechanical hardening treatment.

The present viewpoint paper emphasizes on harnessing the local fluctuations in chemical composition in HEAs on the spatial configurations of crystallographic defects to trigger simultaneously diverse strengthening effects that would typically be difficult to achieve in dilute/conventional alloys. The following key takeaways and recommendations are proposed:

Solute strengthening in HEAs is largely predicted based on random atomic arrangement, wherein the lattice friction effect is the sole criteria for strengthening of dislocation motion. However, experimental single-phase HEA microstructures largely deviate from such assumption in terms of compositional heterogeneities inherent to these alloys. Greater efforts are needed to appraise such chemically driven ordering and their corresponding influence on roughening dislocation dynamics. Noteworthy are the attempts already been made by Zhang et al. [71] in this direction, wherein they recently introduced a stochastic Peierls-Nabarro (PN) model that considers the role of short range ordering effect as well.

1) When juxtaposing single-phase HEAs against dual/multi-phase HEAs in light of mechanical response, the superiority of the latter is clearly visible. This is owing to the additional room for

tailoring multiscale defect/phase heterogeneities in multi-phase HEAs stemming from aggravating local chemical gradients.

- 2) Multi-phase HEAs provide opportunities for structural application oriented design. Spinodally modulated structures are critical for augmenting strengthening, especially in case of refractory applications. On the other hand, ordered precipitation hardening pathway provides greater synergy between strength and ductility. On mesoscopic scales, creation of crystallographically dissimilar interphase boundaries can be utilized to activate interfacial strengthening mechanisms.
- 3) Novel design schemes involving hierarchical microstructures with simultaneous compositional fluctuation, grain size and defect topology gradients can be employed to promote multi-scale strengthening in new generation HEAs. Fig. 3 illustrates a schematic of such model hierarchical structures utilizing compositional gradients.

Finally, the current viewpoint beckons upon a greater emphasis on metal physics based microstructural engineering in multicomponent alloys rather than solely focusing upon exploration of new compositions that seems to be a limitless pursuit.

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